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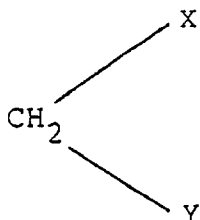
Applicant: **PRESIDENZA DEL CONSIGLIO DEI
MINISTRI -UFFICIO DEL MINISTRO PER IL
COORDINAMENTO DELLE INIZIATIVE PER LA
RICERCA SCIENTIFICA E
TECNOLOGICA 76, Lungotevere Thaon di
Revel
I-00100 Roma(IT)**

Inventor: **Santi, Roberto, Dr.
24F, Piazza delle Armi
I-28100 Novara(IT)**
Inventor: **Cometti, Guiseppe
14, via Crocetta
I-28048 Verbania Pallanza, Novara(IT)**

Representative: **Barz, Peter, Dr. et al
Patentanwälte Dipl.-Ing. G. Dannenberg Dr.
P. Weinhold, Dr. D. Gudel Dipl.-Ing. S.
Schubert, Dr. P. Barz Siegfriedstrasse 8
D-8000 München 40(DE)**

Catalytic process for preparing ethylene-tetracarboxylic esters.

Process for preparing ethylene-tetracarboxylic esters by dimerization of malonic compounds of the formula:

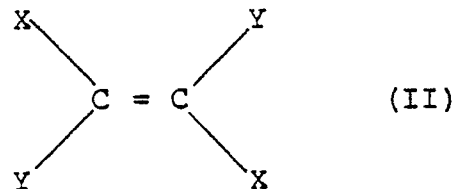
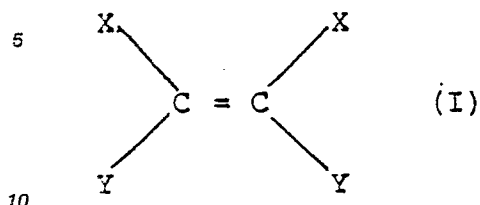


wherein $\text{X} = \text{COOR}$, $\text{Y} = \text{COOR}'$ and R and R' represent an organic group, characterized in that the dimerization is an oxidative dimerization conducted in the presence of a catalyst consisting of the salt of a transition metal.

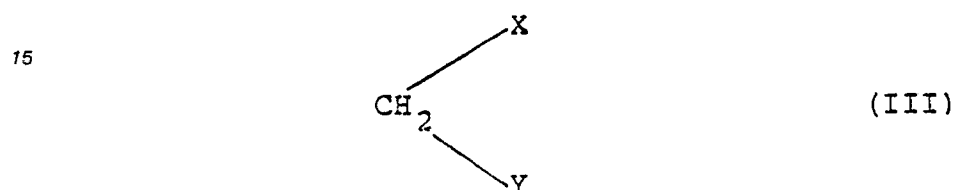
EP 0 330 203 A1

CATALYTIC PROCESS FOR PREPARING ETHYLENE-TETRACARBOXYLIC ESTERS

The present invention relates to a process for preparing ethylene-tetracarboxylic esters of the formula (I) or (II):



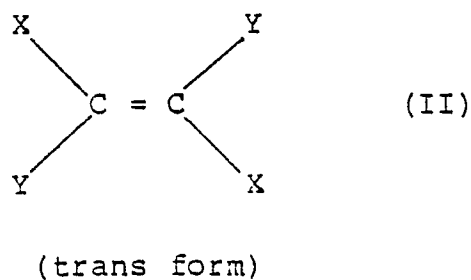
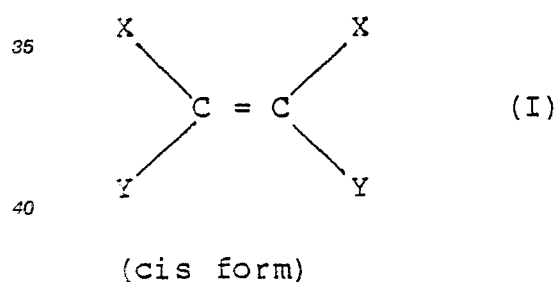
starting from malonic compounds of the formula (III):



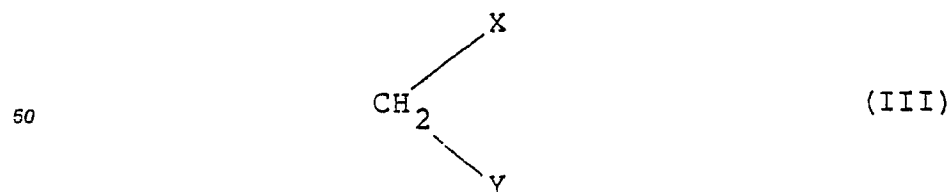
wherein $\text{X} = \text{COOR}$, $\text{Y} = \text{COOR}'$ and R and R' , the same or different, are organic groups, inert under the synthesis conditions. There are known methods of preparing esters of the formula (I) or (II), where $\text{X} = \text{Y} = \text{COOR}$ and where R is an alkyl group, starting from malonates and NaOH (25% b.w.) in CH_2Cl_2 , containing tetrabutylammonium bromide and trichlorobromomethane (see German Patent 3,031,348), or by electrolytic dimerization the malonate (see U.S. Patents 4,076,601 and 4,659,441); these ethylene-tetracarboxylic esters can be used in detergent formulations or for the production of technopolymers. Furthermore, they can be transformed into pinacol derivatives by catalytic hydroxylation with hydrogen peroxide.

The Applicants have now found that it is possible to obtain the same esters by an alternative simpler, quicker and more advantageous process.

In its widest aspect, the invention relates to a catalytic process for preparing ethylene-tetracarboxylic esters of formula (I) or (II):



45 by dimerization of malonic compounds of formula (III):



wherein $\text{X} = \text{COOR}$, $\text{Y} = \text{COOR}'$ and R and R' , the same or different, represent an organic group inert

under the synthesis conditions; the process is characterized in that the dimerization is an oxidative dimerization, which is carried out by the use of oxygen (or another gas containing oxygen), in the presence of a catalyst consisting of an inorganic (for instance nitrate) or organic salt of a transition metal preferably selected from manganese, cobalt and copper.

5 Very good results are attained if the work is carried out under anhydrous conditions and in the presence of an organic salt of an alkali metal or of an alkaline earth metal and if the synthesis is performed at 30-200 °C, in a polar solvent, which can solubilize the catalyst. The pressure is preferably between atmospheric pressure and 50 bar; the space velocity of the oxidizing gas (oxygen, air, enriched air, poor air or other gases) is at least 2 Normal-litres/h per liter of reacting volume.

10 The above mentioned groups R and R' of formula (I) and (II) may represent, for instance, alkyl, cycloalkyl, aryl or heterocyclic groups (optionally substituted), containing from 1 to 18 C atoms. As an alkyl group we mean also an arylalkyl group, a (cycloalkyl)alkyl group or an alkyl group substituted with heterocyclic groups, containing O, N or S in the ring; as an aryl group we mean also an alkyl-aryl group, a cyclo-alkyl-aryl group or an aryl group substituted with said heterocyclic groups; as a cycloalkyl group we mean also an alkyl-cycloalkyl group, an aryl-cycloalkyl-group or a cycloalkyl group substituted with said heterocyclic groups; as a heterocyclic group we mean also an alkyl-, cycloalkyl-, or aryl-heterocyclic group.

Generally, the catalyst is selected from the Mn, Co, Cu salts of carboxylic acids containing from 1 to 22 C atoms; among these salts acetates are preferred; the same catalyst may be used in very little amounts, generally between 0.030 and 0.001 mols of metal (contained in the catalyst) for each mol of the desired tetracarboxylic ester. The polar solvent in which the catalyst dissolves is preferably selected from the aliphatic carboxylic acids containing up to 5 C atoms, in particular acetic acid.

The reaction conditions can be easily maintained under the anhydrous state by adding an anhydride, preferably acetic anhydride. The alkali metal or alkaline earth salt (to be used together with the catalyst) can be advantageously the salt of a carboxylic acid containing from 1 to 22 (and better from 1 to 10) carbon atoms and it can be preferably the sodium salt of acetic acid. Obviously, the reaction temperature (from 30 to 200 °C) is depending on the composition of the reaction mixture and on the desired reaction rate. At the end of the synthesis, the ester of formula (I) is separated, upon distillation of the solvent, by an usual technique, such as for example the extraction by means of organic solvents, followed by precipitation.

It is also advantageous to recover the catalyst from the reaction mixture and to recycle it into the reaction system.

The process of the present invention allows one to obtain the compounds of the formula (I) and (II) with good yields, with a good control of the reaction and therefore by a simple and economic method; therefore, it can be exploited in many an industrial preparation.

Some examples follow to illustrate the invention without limiting the same invention.

EXAMPLE 1

Into a glass reactor provided with agitator, condenser and a control system for the temperature and for the oxygen feed, were loaded:

1 g (0.0037 mols) of $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$
 20 g (0.244 mols) of anhydrous CH_3COONa
 35 g (0.219 mols) of diethyl malonate
 33 cm³ of acetic acid
 45 50 cm³ of acetic anhydride

Into the mixture 10 litres/h of oxygen were allowed to bubble, while keeping the reaction mixture at 100 °C by means of an external oil bath; after 8 hours, at the end of the reaction, the solvents were removed and a fraction was obtained which contained:

3.0 g (0.018 mols) of diethyl malonate;
 50 1.9 g (0.011 mols) of diethyl ketomalonate;
 29.5 g (0.093 mols) of 1,1,2,2-tetraethyl-ethylene-tetracarboxylate.

Therefore, the tetraethyl-1,1,2,2-ethyl enetetracarboxylate was obtained with a 85% yield.

55 EXAMPLE 2

Into the same reactor of example 1 were loaded:

1 g (0.0037 mols) of $\text{Mn}(\text{CH}_3\text{COO})_3 \cdot 2\text{H}_2\text{O}$

20 g (0.244 mols) of anhydrous CH_3COONa

60 cm^3 of tert. butyl alcohol

40 cm^3 of acetic anhydride

Into the mixture 10 litres/h of oxygen were allowed to bubble, while keeping the reaction mixture at a lower temperature (80°C) by means of an external oil bath; after 8 hours, when the reaction was completed,

solvents were removed and a fraction containing:

9.2 g (0.057 mols) of diethyl malonate;

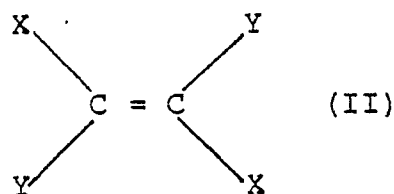
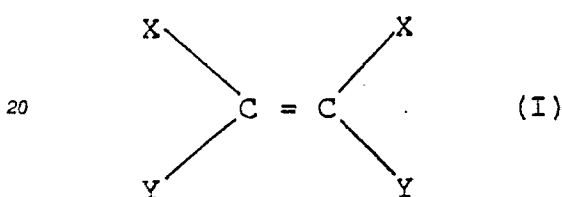
2.5 g (0.014 mols) of diethylketomalonate;

22.13 g (0.070 mols) of tetraethyl-1,1,2,2-ethylenetetracarboxylate;

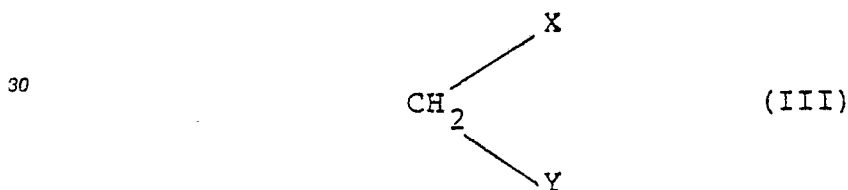
was obtained; the yield was 64%.

Claims

1. Process for preparing ethylene-tetracarboxylic esters having the formula (I) or (II):



starting from compounds of the formula (III)



wherein $\text{X} = \text{COOR}$, $\text{Y} = \text{COOR}'$, R and R' being the same or different, represent an organic group, inert under the synthesis conditions, characterized in that the dimerization is an oxidative dimerization which is performed by use of oxygen (or of another oxygen containing gas), in the presence of a catalyst consisting of the inorganic or organic salt of a transition metal preferably selected from manganese, cobalt and copper.

2. Process according to claim 1, wherein the dimerization is performed at $30\text{--}200^\circ\text{C}$, under anhydrous conditions, preferably maintained by addition of an anhydride (such as acetic anhydride), in the presence of an organic salt of an alkali metal or of an alkaline-earth metal, in particular a salt of a carboxylic acid containing from 1 to 22 (preferably from 1 to 10) carbon atoms, such as for instance acetic acid.

3. Process according to claim 1 or 2, wherein the dimerization is performed at a pressure comprised between the atmospheric pressure and 50 bar, in the presence of a polar solvent (organic), preferably selected from the carboxylic acids containing from 1 to 5 carbon atoms, in particular acetic acid.

4. Process according to anyone of the preceding claims, wherein the space velocity of the oxidizing gas is equal to or higher than 2 normal-litres/h for each liter of reacting volume.

5. Process according to anyone of the preceding claims, wherein the mentioned inert groups R and R', in formulae (I), (II) and (III), represent alkyl, cycloalkyl, aryl or heterocyclic groups, optionally substituted, containing from 1 to 18 C atoms.

6. Process according to anyone of the preceding claims, wherein the catalyst is selected from the salts derived from a carboxylic acid containing from 1 to 22 C atoms and from a transition metal selected from Mn, Co and Cu, the amount of catalyst (expressed as pure metal) being from 0.030 to 0.001 mols for each mol of tetracarboxylic ester.

7. Process according to anyone of the preceding claims, wherein the tetracarboxylic ester is separated, at the end of the synthesis and upon distillation, from the organic solvent, by extraction with an organic solvent followed by precipitation.

8. Use of the ethylene-tetracarboxylic esters, obtained according to the process described in anyone of the preceding claims, in the field of detergent formulations.

9. Use of the ethylene-tetracarboxylic esters, obtained according to the process described in anyone of claims from 1 to 8, for the manufacture of technopolymers.

5 10. Use of the ethylene-tetracarboxylic esters, obtained according to the process described in claims from 1 to 8, for the synthesis of pinacol derivatives by catalytic oxidation with H_2O_2 .

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89103198.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁴)
D,A	DE - A1 - 3 031 348 (HOECHST AG) * Claims * --	1	C 07 C 69/604 C 07 C 67/343
D,A	US - A - 4 076 601 (D.A.WHITE) * Claims * --	1	
A	CHEMICAL ABSTRACTS, vol. 93, no. 9, September 1, 1980, Columbus, Ohio, USA Y.HORI et al. "Studies on the application 1,8-diazabicyclo[5.4.0]-undec-7-end (DBU). I. Chlorination and dimerization of active methylene compounds by DBV-CCl ₄ reagent." page 643, right column, abstract-no. 95 231h & Rikogakubu Shuho 1978, 6, 19-22 ----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. ⁴)
			C 07 C 67/00 C 07 C 69/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 17-05-1989	Examiner HOFBAUER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			